Structural relationship between humic fractions from peat and lignites from the Miocene Granada basin

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Fulvic acids, humic acids and humins, isolated from two closely situated peat and lignite deposits, have been examined by solid-state ^{13}C n.m.r. and analytical pyrolysis. No marked structural differences were found between the humic fractions from the various deposits, suggesting a common origin. Within each deposit some distinguishing structural characteristics were observed between the humic fractions. The differences observed showed that the loss of carbohydrate and lignin during the early coalification process led to the accumulation of a predominantly polyalkyl, kerogen-like residue. The humin fractions from both materials contain the greatest amounts of aromatic structures, although they also present high proportions of aliphatic components. Thus, their n.m.r. spectra consist almost exclusively of alkyl and aromatic hydrocarbon entities. This agreed with the results of pyrolysis, which reflected the presence in humins of condensed alkyl material.

(Keywords: structural relationship; humic fractions; peat)

Diverse recent sediments, such as algal mats and aquatic or sapropelic sediments, have been used as model systems for studying the formation of ancient sediments and the fate of biopolymers in the course of their diagenesis. As a result of such studies, the macromolecular solvent–insoluble portion of organic material present in such deposits, sometimes referred[1] to as 'protokerogen', has been postulated as a precursor of kerogen in older sediments[2,3], although no direct evidence has been presented.

Immature low rank coals, derived chiefly from terrestrial plants, may constitute a suitable environment to investigate the above process. They contain a high proportion of colloidal humic materials, including a fraction insoluble in organic solvents and in acid and alkaline solutions, similar in operational terms to the humin isolated from soils. Based on both its behaviour during chemical degradation and its capability to retain trapped hydrocarbons, Hayatsu *et al.*[4] suggested a similarity between this humin from low rank coals, which they call kerogen-like material, and kerogen from more mature rocks.

At the same time, the characterization of the humic acid (HA) fraction from coals has been shown to be useful for obtaining information about the organic source materials and depositional environments[5,6], and for the elucidation of diagenetic pathways during the coalification process[7]. Some recent publications on the characterization of humic fractions from brown coals by spectroscopic and degradative methods have addressed the above topics[8,9].

The present study explored the structural features of the humic fractions (humic, fulvic acids and humins) isolated from two closely situated low rank coals in the Miocene Granada basin (Southern Spain), which may constitute a peat–lignite transition model, similar to that described by Given[10]. In addition, advantage has been taken of a peculiar property of the coals studied, i.e. the relatively high amount of fulvic acids (FA), seldom studied in coal samples. As shown in a previous work on their biomarker distribution[11], there is a maturity gradient in these low rank coal deposits.

The aim of this work is to demonstrate a diagenetic relationship between the three humic fractions that could be interpreted in terms of the direct formation of kerogen-like materials from soluble humic substances or vice versa. In addition, structural comparison of these fractions may contribute to the understanding of the fate of depositional organic matter during coalification.

The structural characteristics of the different humic fractions have been approached by non-destructive spectroscopic methods (FT-i.r. and CP/MAS ^{13}C n.m.r.) and pyrolysis-g.c.–m.s., widely used for the structural characterization of insoluble humic substances from different sources.

MATERIALS AND METHODS

The lignite samples were taken at different depths (ARL-A at 1.5 m, and ARL-B at 3.5 m) of the Arenas del Rey deposit in the Miocene Granada basin (Southern Spain), and the peat sample (PP) from the nearby Padul deposit. Various chemical, geochemical and geological data of the parent low rank coals have been published elsewhere[11,12].

The peat and lignite samples were ground to less than

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53 μm and Soxhlet extracted with toluene for 48 h. The bitumen-free samples were then extracted three times with 0.1 M NaOH solutions. The extracts obtained after centrifugation were precipitated with 0.1 M HCl. The HA were centrifuged, dialysed against distilled water and freeze-dried. The FA were extracted and purified according to the procedure reported elsewhere for soil FA[13]. The humin or kerogen-like fraction (the organic matter left after extraction of the bitumen and alkali soluble humic substances) was subjected to demineralization according to the procedure outlined by Durand[14]. Finally, the residues were washed, dialysed against distilled water and freeze-dried.

The elementary composition of the parent materials and their humic fractions was determined using a CHN microanalyser.

The FT-i.r. spectra were obtained from KBr pellets (1 mg of sample per 200 mg of KBr) by co-adding 100 scans at a resolution of 2 cm^{-1}.

High resolution solid-state ^{13}C n.m.r. spectra of the samples were collected at 75.4 MHz under cross polarization–magic angle spinning conditions (CP/MAS) using the quantitative acquisition conditions described elsewhere[15].

Analytical pyrolysis (Py) was carried out at 700°C in a pyroprobe unit consisting of a Pt coil heated at a rate of up to 20°C ms^{-1}. The sample (2 mg) was placed in a quartz tube, using quartz wool for end plugs. The volatile pyrolysis products were collected in a liquid N_2 cold trap system, recovered with *n*-hexane and analysed by g.c. and g.c.–m.s. in instruments equipped with a 25 m cross-linked fused silica column (i.d. 0.32 mm) coated with OV-101 (0.11 μm film thickness). The g.c. oven was heated from 40 to 300°C at a rate of 6°C min^{-1}. The Py products were identified by studying the m.s. patterns, and confirmed by comparing with mass spectra and g.c. retention times of standards.

RESULTS AND DISCUSSION

As expected from their low degree of maturity, the samples chosen contain a high proportion of humic fractions (83–88 wt% HA, 3–5 wt% FA, 7–14 wt% humins). There were noticeable amounts of FA, virtually lacking in most coal samples.

Table 1 shows the elemental analysis and atomic ratios of the parent coals and their respective humic fractions. The large contribution of the HA to their parent coals is reflected in the similarity between both groups of data. As expected, in the three materials studied, the atomic H/C vs. O/C ratios suggests a progressive increase in aromaticity and decrease in the amounts of oxygen-containing functional groups in the order FA > HA > Hum.

In any case, because of their intrinsic chemical complexity the elementary composition data of these materials can only be interpreted in a very general way.

Due to the great similarity in composition of the samples ARL-A and ARL-B, they will be discussed together.

The FT-i.r. of the samples PP and ARL-A and their respective humic fractions (not shown here) were remarkably similar and rather featureless. In particular, the spectra of the bulk samples are virtually identical with that of the HA fractions, most likely again as a result of the predominance of this fraction in the samples.

Major adsorption bands due to OH and aliphatic C–H stretching at around 3400 and 2920 cm^{-1} are prominent in all the fractions. The stronger acidic character of the FA was reflected by the intensity of the carboxyl vibration at 1720 cm^{-1}. Only vaguely defined bands assigned to aromatic C=C (1510 cm^{-1}) were apparent in the parent samples.

Figure 1 shows CP/MAS ^{13}C n.m.r. spectra of the humic fractions isolated from the peat (PP) and lignite ARL-A samples. Relative amounts of the different carbon types present in the samples, as determined from the integration of spectral regions according to classical subdivisions, are given in *Table 2*.

The n.m.r. spectra are dominated by broad signals assigned to aliphatic (0–100 ppm) and unsaturated carbons (110–160 ppm) and resonances around 175 ppm ascribed to esters and/or carboxyl carbons. Only in the sample PP are resonances for heteroatom-substituted aromatic carbons (145 ppm) more prominent in the HA spectra than in the parent material. However, no discernible trace of lignin (sharp methoxyl signal at

Table 1 Elemental composition (wt%) and atomic ratios (wt%) of the parent coals (PP = Padul peat, ARL = Arenas del Rey lignites) and their different humic fractions (dry, ash-free basis)

	C	H	N	O+S[a]	H/C[b]	O/C[b]	Ash
PP bulk	50.3	5.1	2.3	42.3	1.2	0.6	19.2
FA-PP	48.9	5.8	1.2	43.9	1.4	0.6	1.9
HA-PP	53.0	4.9	1.3	38.7	1.1	0.5	3.5
Hum-PP	61.6	1.9	0.3	36.2	0.3	0.4	nd
ARL-A bulk	55.9	4.0	2.4	37.7	0.8	0.5	25.5
FA-ARL-A	51.0	5.3	1.4	42.1	1.2	0.6	1.1
HA-ARL-A	58.6	4.5	2.4	34.5	0.9	0.4	5.8
Hum-ARL-A	62.1	2.3	0.9	34.7	0.4	0.4	nd
ARL-B bulk	58.9	3.8	4.1	32.3	0.7	0.4	nd
FA-ARL-B	51.5	5.6	1.8	41.0	1.3	0.6	1.5
HA-ARL-B	59.2	4.1	2.0	34.6	0.8	0.4	3.5
Hum-ARL-B	61.8	1.1	0.7	36.3	0.2	0.4	nd

[a] By difference
[b] Atomic ratios
nd = Not determined

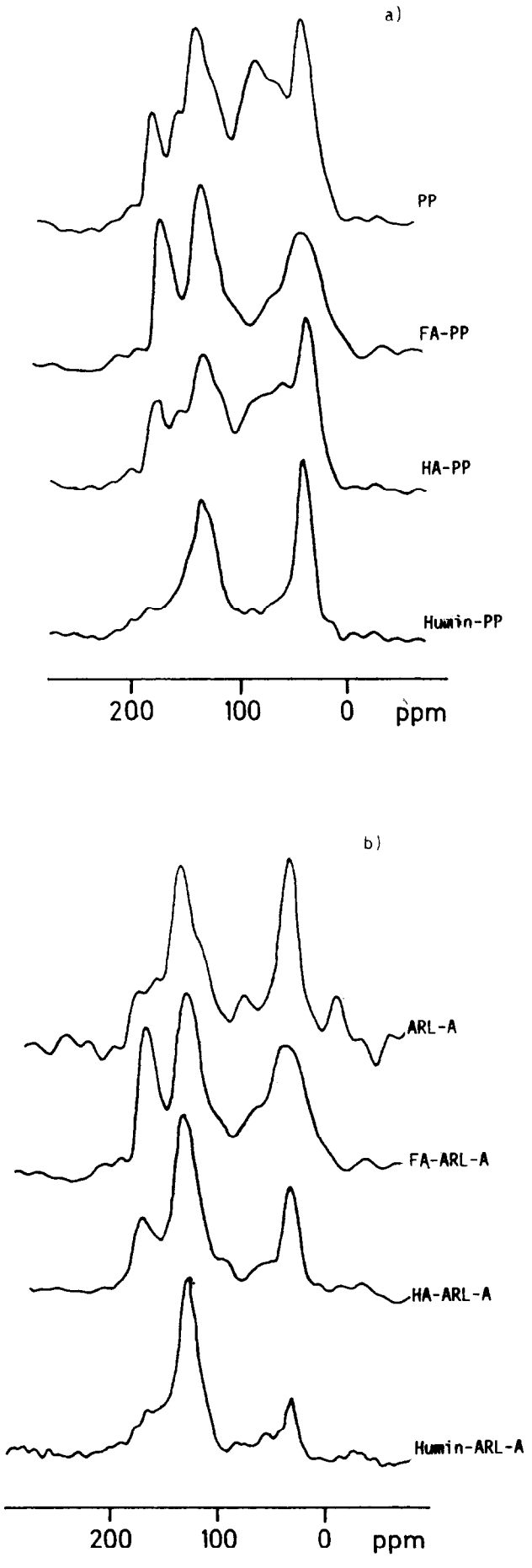


Figure 1 CP/MAS ^{13}C n.m.r. spectra of (a) the Padul peat (PP) sample, and (b) the Arenas del Rey (AR-A) lignite sample, and their fulvic acid, humic acid and humin fractions

55 ppm) or carbohydrate structures (distinct signals at 64, 72–76, 84–90, 106 ppm) were apparent.

The HA from PP and ARL samples showed CP/MAS ^{13}C n.m.r. spectra typical of HA from low rank coals, dominated by aromatic carbon resonances in the 110–160 ppm region and aliphatic carbons in the 0–40 ppm region. There is a step progressive decrease in the signal intensities in the O-alkyl aliphatic region (carbohydrates and methoxyl groups) in the sequence PP > ARL-A > ARL-B, as well as a significant decrease of the shoulder at 145–150 ppm (O-aryl) due to possible loss of phenols and aromatic ethers. The spectra seem to reflect the fact that these samples constitute a chronological sequence within the typical steps of the coalification process. Similar trends have been observed in buried fossil woods[16]. Signals near 175 ppm, assigned to C in carboxyl groups, are also observed in the spectra of HA and FA. The latter are also characterized by prominent O-alkyl bands. The spectra of humin fractions show broad signals in the aromatic and aliphatic regions, the former being more pronounced. The contribution to coal humin composition of recalcitrant condensed polyalkyl structures has been confirmed by FT-i.r. and chemical degradation[17].

The values for the carboxyl group contents seem to be overestimated, exceeding the classical estimations of total acidity. Similar results have been found by other authors[18,19]. This suggests that either the ^{13}C n.m.r. carboxyl region could include other types of carbon atoms, or that only the most 'external' carboxyl groups are accessible to the classical wet (titration-based) chemical methods.

The aromaticity, estimated by quantification of the aromatic region, does not follow the regular trend expected from the presumable similarity between these samples. In all cases the humin fractions were the most aromatic. The high proportion of aromatic carbons in lignite samples and their fractions has been considered to be due to the high content of the inertinite maceral (20 vol%), i.e. a wood pyrolysis product with a high content of polycyclic aromatic components[20]. HA from the PP sample contain a lower proportion of alkyl carbons (0–46 ppm region) than those from lignites, but the total amount of aliphatic carbons (0–103 ppm) is higher in the former.

The considerable amount of saturated alkyl structures in the insoluble residues agrees with the results reported for humins separated from soils[21]. This suggests the accumulation and/or formation of refractory alkyl polymers having resistance to geological degradation, similar to that of the altered lignins traditionally considered as major precursors of the lignite fractions.

Pyrograms of the different humic fractions from the ARL-A lignite are presented in *Figure 2*. They are representative for all the samples studied. The different peak numbers correspond to compounds listed in *Table 3*. Since a detailed description of the pyrolysis products is not required to characterize the differences between the samples, *Table 3* shows only the main series of compounds present in each pyrogram and only representative peaks are labelled in *Figure 2* to illustrate the nature of the Py products.

Most of the major compounds are well known typical pyrolysis products from various biopolymers, such as polysaccharides, proteins, lignins and lipid biopolymers[22–25]. Dialkyl phthalates were also frequently encountered.

Table 2 Integration values for the different regions of the ^{13}C n.m.r. spectra of the parent coals and their humic fractions

	0–46 ppm	46–110 ppm	110–160 ppm	160–210 ppm
PP bulk	26.2	33.8	28.3	11.7
FA-PP	21.5	26.7	34.7	17.1
HA-PP	25.3	33.6	29.4	11.7
Hum-PP	24.0		65.1	
ARL-A bulk	34.1	21.5	40.1	4.8
FA-ARL-A	19.7	26.2	35.4	16.5
HA-ARL-A	18.5	15.3	51.1	15.1
Hum-ARL-A	18.1		66.8	
ARL-B bulk	30.8	20.9	38.5	9.7
FA-ARL-B	13.7	28.0	37.6	20.6
HA-ARL-B	30.9	21.9	36.9	10.2
Hum-ARL-B	19.4		70.9	

Table 3 Semiquantitative abundance of the pyrolysis products identified in the different samples

Py products	PP			Lignites		
	FA	HA	Humin	FA	HA	Humin
Alkanes/alkene pairs	+	++	+++	+	++	+++
Long chain products	–	–	+	–	+	+
Isoprenoid hydrocarbons	–	++	++	–	+	+
Phenol	++	++	++	++	++	++
C1 phenols	++	++	++	++	++	+
C2 phenols (122)[a]	+	+	–	+	+	–
C3 phenols (136)	++	+	–	+	+	–
Catechol	+++	++	+	+++	++	+
Methoxy phenols (124)	++	+	–	++	–	–
Di-methoxy phenols (154)	++	++	++	++	+	+
Phthalates	++	+	++	++	+	+
N-bearing compounds	+	+	+	+	+	+
Furan derivatives	++	+	–	++	+	–

+, ++, +++: low, medium, high relative abundances
[a]Single ions monitorized for quantitation fo some homologue series are indicated in parentheses

Noticeable qualitative and quantitative differences between the pyrolytic patterns were observed. All the samples yielded complex pyrograms, which is unusual for FA from other origins[26].

Furan derivatives arising from carbohydrates, as well as styrene, pyridines, pyrroles, benzonitriles and indols similar to those derived from peptidic materials, were released in high amounts in the pyrolysis of the peat HA. This suggests the presence of similar biopolymers in their structure, as corresponds to the recent contribution of plant and microbial inputs to the peat[11]. In the lignite HA (*Figure 2b*) only trace amounts of furfural were detected, indicating that polysaccharides and proteins are progressively lost with increasing coalification. Similar results were found by other authors studying buried woods[27,28] or peat formation[29].

The most abundant pyrolysis products were an homologous series of n-alkanes and n-alkenes with chain lengths up to C_{30}. These aliphatic hydrocarbons were also observed as major components in peat and coal pyrolysates[30,31] and indicate the presence of significant amounts of condensed polyalkyl components.

As previously suggested for similar materials[32,33], the major contributors to the alkyl components in peat and lignite might be new types of non-saponifiable, highly aliphatic biopolymers similar to those recently identified in present-day and fossil plant cuticles[25] and in the cell walls of some algae species[34]. Such substances yield, by flash pyrolysis, a series of *n*-alkanes, *n*-alk-1-enes and α,ω-alkadienes with a distribution similar to those found in our HA samples. Although the above biopolymers are minor constituents of the original biomass, they are more refractory than other major vegetable components including lignin[32] and could concentrate in the sediment during early diagenesis.

Acyclic isoprenoid hydrocarbons, such as prist-1-ene, prist-2-ene and phytadiene, were also identified in higher amounts in peat than in lignites. The phytol side-chain of chlorophyll in photosynthetic organisms can be the source of phytadienes[35]. On the other hand, pristenes could arise from tocopherols, since flash pyrolysis of α-tocopherol yields prist-1-ene as major product[36].

Additional aliphatic series identified in the pyrograms were fatty acids from C_{14} to C_{16} and methylketones from C_{24} to C_{27}. These compounds might arise from the thermal vaporization of lipids 'trapped' in the macromolecular matrix of the HA[37] and humins (unpublished

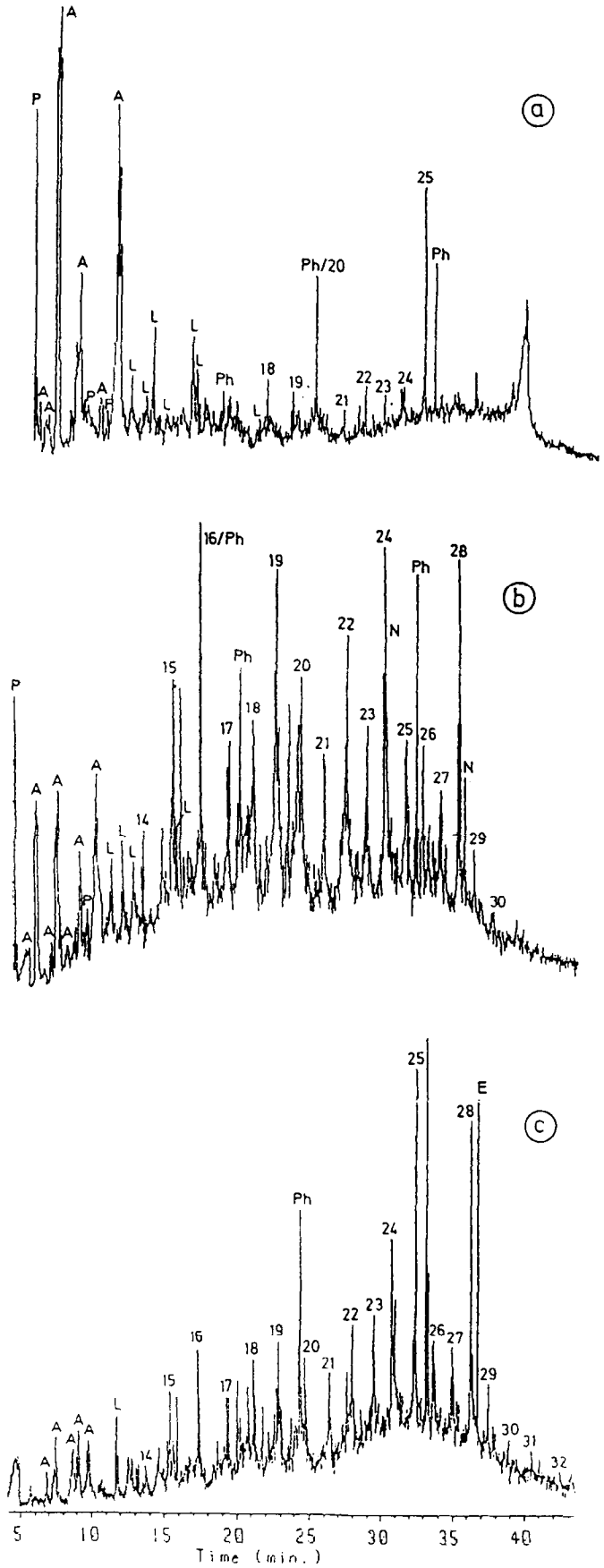


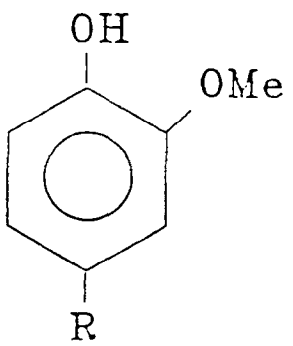
Figure 2 Total ion chromatographs (TIC) of the pyrolysis products from (a) the fulvic acid, (b) humic acid, and (c) humin fractions of the ARL-A sample. Numbered peaks denote chain length of *n*-alk-1-ene and *n*-alkane pairs. A, aromatic compounds; P, carbohydrate-derived compounds; L, typical lignin-derived phenolic compounds derived from lignin; Ph, dialkyl phthalates; N, octadecenamides; E, unidentified long chain compounds

results) and are, therefore, not necessarily primary pyrolysis products.

Other diagnostic groups of pyrolysis products in peat were phenolic compounds, characteristic for lignin pyrograms[23,38], although they have also been found as minor pyrolysis products of proteins[22], polycarboxylic acids[39] and carbohydrates[24]. Due to its high resistance to biodegradation, lignin has frequently been detected in geological materials by different procedures, and considered as a source indicator of terrestrial plant inputs[36,40].

The major lignin pyrolysis products identified in the peat pyrolysate were guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol and lower amounts of *trans*-isoeugenol, acetoguaiacone and coniferyl alcohol, all potentially derived from guaiacyl units predominant in hardwood lignins (*Figure 3*). This result agrees with the detection of terpenoid biomarkers typical of conifers in the bituminous fractions[11]. A small amount of 2,4-dimethoxyphenol was also detected. The lack of syringly structures in the pyrograms seems to indicate the minor contribution of angiosperms to these materials. The detection of C_6–C_3 units suggests that lignin is only partially degraded. On the other hand, the absence of oxidized phenols in peat pyrolysates could reflect an anoxic burial history, in agreement with previous pyrolysis studies on the influence of burial on wood[27,28].

Phenolic compounds have not been detected in significant amounts in the lignite pyrograms. However,



R	Compound
H	Guaiacol
CH_3	4-methylguaiacol
CH_2CH_3	4-ethylguaiacol
$CH{=}CH_2$	4-vinylguaiacol
OCH_3	2,4-dimethoxyphenol
$CH{=}CHCH_3$	trans-isoeugenol
$COCH_3$	acetoguaiacone
$CH{=}CHCH_2OH$	coniferylalcohol

Figure 3 Structures of guaiacol derivatives found in the pyrograms

it cannot be concluded that lignin does not survive the coalification process. In fact, as revealed by chemical degradative methods[9], variations in the proportions of phenolic groups presumably reflect variations in the composition of the original plant lignin, rather than changes due to the coalification process.

According to Hatcher *et al.*[27], as coalification increases, the lignin structural units are transformed into catechol structures. However, this trend was not observed in our lignite samples, where only phenols were identified but in minor amounts. Thus, the lower amounts of phenol, cresols and other phenolic compounds in ARL-A HA pyrolysate might reflect the alternative contribution to these lignites of planktonic material, which does not normally contain lignin[24]. This result is supported by the study of the bituminous fraction, which showed a contribution of marine material in the formation of this lignite[11].

Figure 2c shows a typical pyrogram of the kerogen-like residue (humin fractions) isolated from the samples. The principal characteristic is the presence of an homologous series of *n*-alk-1-enes and *n*-alkanes up to C_{30}, confirming the presence of the major polyalkyl entity suggested from spectroscopic methods. This is in agreement with previous findings on similar materials[30,41]. This aliphatic entity may derive in part from resistant biogenic and/or catagenic highly aliphatic biopolymers.

Finally, prist-1-ene and prist-2-ene were also identified in humin pyrolysates. The presence of such compounds in the whole coal and humin pyrolysates and their lack in the bituminous fraction suggests pristane being chemically bonded to the coal matrix[42].

CONCLUSIONS

The structural characteristics of soluble and insoluble humic fractions from immature coals provide useful information on coal source materials as well as on their diagenetic history.

From the pyrolysis and CP/MAS ^{13}C n.m.r. results it can be concluded, in agreement with Stout *et al.*[29], that the progressive transformation of plant biomass during peat formation and early coalification is dominated by a selective loss of carbohydrate materials and gradual alteration of lignin by depolymerization, dealkylation and defunctionalization. When the geopolymers reach such degrees of transformation, both defunctionalized aromatic and alkyl structures represent the major skeletal units, and have similar resistance to further degradation.

Analysis of the pyrolysis products reveals that conifers were among the original plant material contribution to the sediment, whereas no angiosperm contribution could be detected.

On the other hand, it is suggested that non-hydrolysable macromolecular structures present in protective envelopes of a number of extant organisms, highly resistant to chemical and/or microbial degradation, are enriched during the coalification progress and become incorporated into the humic fractions. However, the catagenic origin from microbial condensation of microbial lipids should not be precluded.

Structural similarity between the humin fractions and typical kerogens suggests a common origin and clear involvement of humic fractions in the formation of kerogen in older sediments.

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